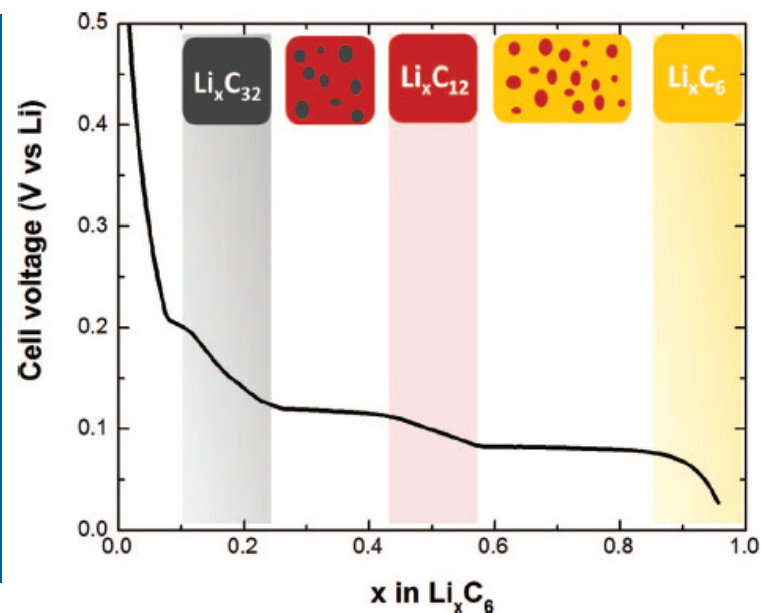


MACROSCALE MODELING FOR FAST CHARGE APPLICATIONS



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U.S. DEPARTMENT OF ENERGY
VEHICLE TECHNOLOGIES OFFICE
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Project ID BAT340

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OVERVIEW

Timeline

- Start: October 1, 2017
- End: September 30, 2020
- Percent Complete: 25%

Budget

- Funding for this Effort:
 - FY18 - \$150K

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
 - Cost, Performance, and Safety
 - Enable Fast Charge Capability

Partners

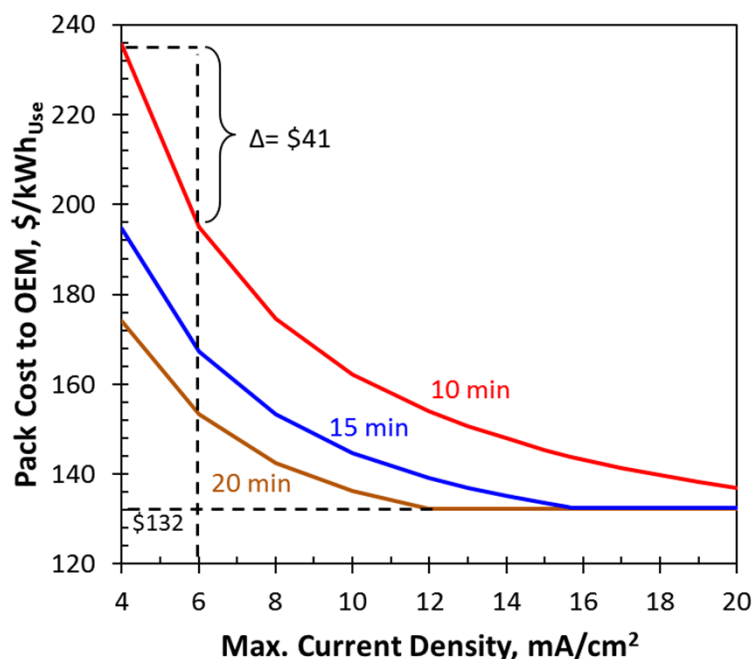
- National Renewable Energy Laboratory
- Idaho National Laboratory
- Argonne National Laboratory

RELEVANCE

Battery Performance and Cost (BatPaC) Model utilized to quantify fast charge challenges.

- The BatPaC model is used to design lithium-ion battery packs and estimate their cost in large volume manufacturing.
- Fast charging BEV battery packs was examined with the BatPaC model.
 - Lithium plating limits the anode thickness and increases pack cost.
 - Cell cost increases nonlinearly with decreasing charging times.
 - Cooling may be needed during charging.
 - Improved electrodes are needed to lower cost.
- The objective of this effort is to extend an existing electrochemical model developed to examine transport, reaction, and phase-change in graphite based electrodes.
- Work is focused on quantifying limitations in the graphite active particles and the SEI that impact the cell's maximum fast charge capability.

<http://www.cse.anl.gov/batpac/>



APPROACH

- In general, the approach for this electrochemical modeling work is to build on earlier successful characterization and modeling studies in extending efforts to fast charge limitations.
- Initial efforts have focused on extending and improving previous electrochemical modeling studies that includes phase-transition phenomena as well as lithium intercalation for graphite active materials.
- The existing model will be improved to better account for high C-rate performance.
- Future electrochemical model development work will focus on the complex SEI structure and lithium plating.

MILESTONE

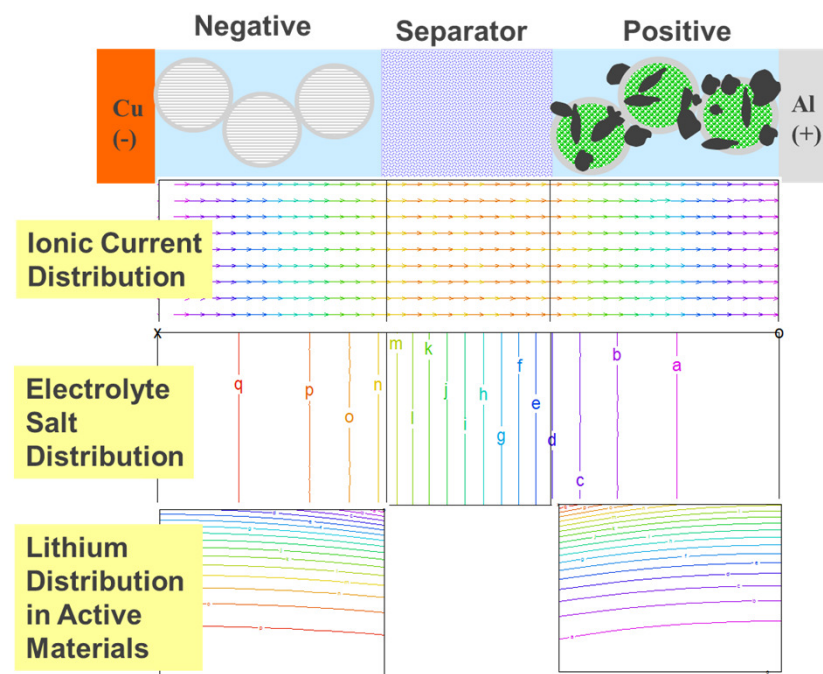
- Improve electrochemical model for graphite to enable fast charge simulation. - Complete

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

- Graphite active materials were shown to be better described with the electrochemical model previously developed that includes the phase-transition phenomena as well as lithium intercalation.
- The graphite electrode electrochemical model was effectively used to simulate Galvanostatic Intermittent Titration Technique (GITT) studies on half-cells.
- Similar modeling results were obtained in comparison to earlier GITT studies on a different type of graphite.
- Applying the advanced electrode model to a broad range of graphite electrode half-cell and reference electrode cell data indicates the lithium diffusion coefficient for graphite is a strong function of applied current (i.e. GITT @ C/18 vs. HPPC @ 3C).
- A single parameter set can be used to simulate the graphite electrode from between around C/5 and 4C.

ELECTROCHEMICAL MODELING

- Electrochemical modeling gives a detailed description of current, potential, and concentration distributions in the cell.
- Differential and algebraic equations describing transport, thermodynamic, and kinetic phenomena occurring in the cell are solved simultaneously.
- Model parameters determined independently.
- Conducted multi-dimensional, multi-scale, and transient simulations.
 - Volume-averaged continuum transport equations
 - Complex solid electrolyte interphase structure
 - Range of active materials studied
- Electrochemical Modeling Applications
 - Associate analytical diagnostic observations with the electrochemical performance changes
 - Identify limiting processes and cell performance optimization
 - Examine degradation and aging mechanisms
 - Guide experimentation



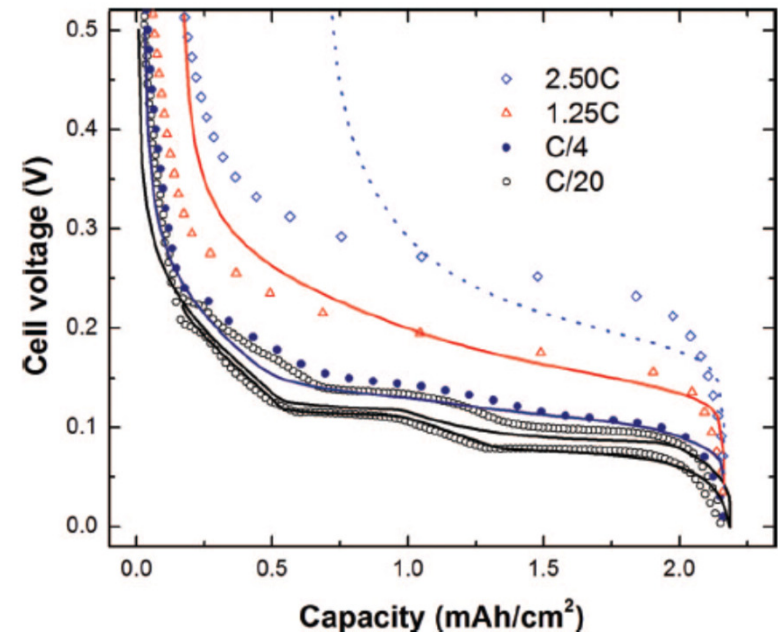
Background Studies and Initial Efforts

- Graphite is known to go through phase changes, also referred to as stages, as lithium is intercalated into it.
- An electrochemical model that accounts for the diffusion of lithium and the phase changes was developed.
- For simplicity three phases were introduced: LiC_{32} , LiC_{12} , and LiC_6 .
- The Avrami equation was used to describe the phase changes.

$$\varepsilon_{s,j} = 1 - \exp(-k' t^n)$$

- The model effectively correlated GITT studies with cycling studies and tracked phase changes during cycling.
- However, the model tended to underestimate the performance at high currents.
- The model was applied to extensive studies with ConocoPhillips graphite (CGP-A12).
- Two planned improvements in model development did not yield significantly better performance at high current rates.

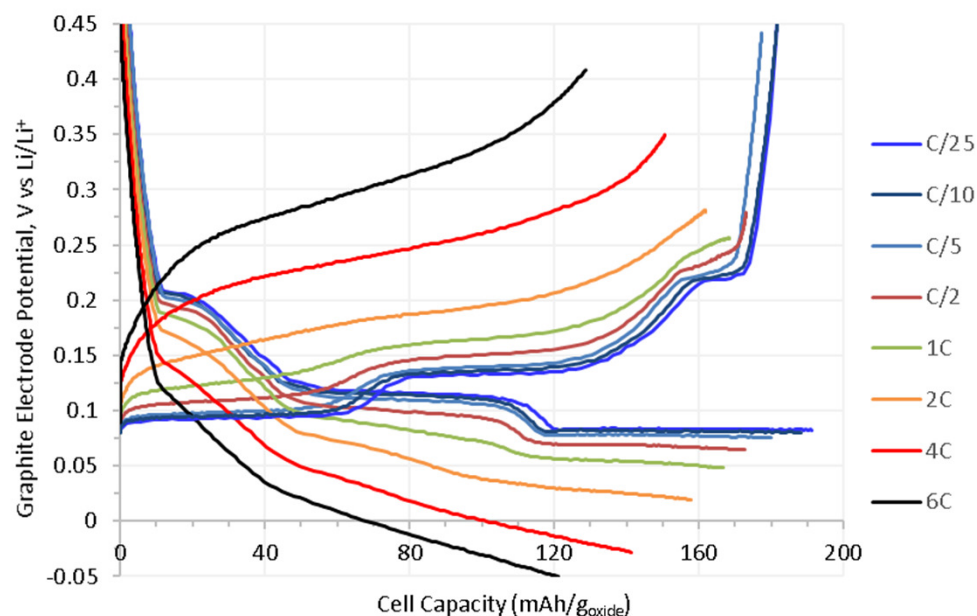
Graphite MCMB/Li Half-Cell Rate Studies



Ref: Gallagher, et al., *J. Electrochem. Soc.*, (2012)

Half-Cell, Full-Cell, and Reference Electrode Cell Studies with A12 Graphite

Negative Electrode Rate Studies for NMC532/Graphite Reference Electrode Cell

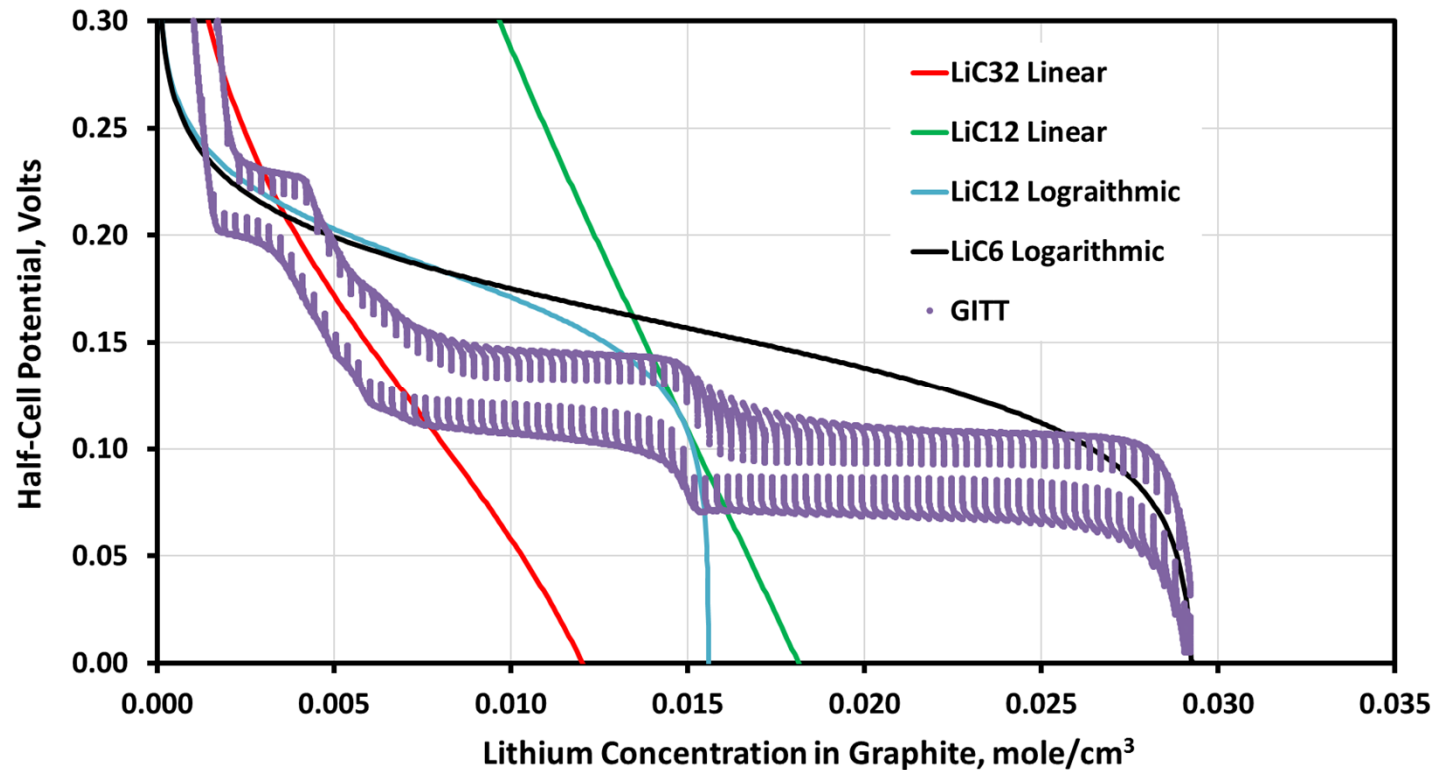


A-A002A(-): made by CAMP
Negative Electrode:
91.8 %wt ConocoPhillips: CGP-A12 graphite
2 wt% C45 (Timcal) + 0.17 %wt Oxalic Acid
6%wt KF-9300 Kureha PVDF binder
5.51 mg/cm ² active loading (A12 graphite + C45)
38.4% electrode porosity
44-μm-thick composite coating
10-μm-thick Cu current collector

- Reference electrode full cell studies include HPPC-like measurements and rate studies.
- Simulations indicate that graphite electrode is not limited by transport of salt in electrolyte during 6C charge.
- Considerable studies with thicker A12 graphite electrodes also available.

Half-Cell GITT Studies on A12 Graphite

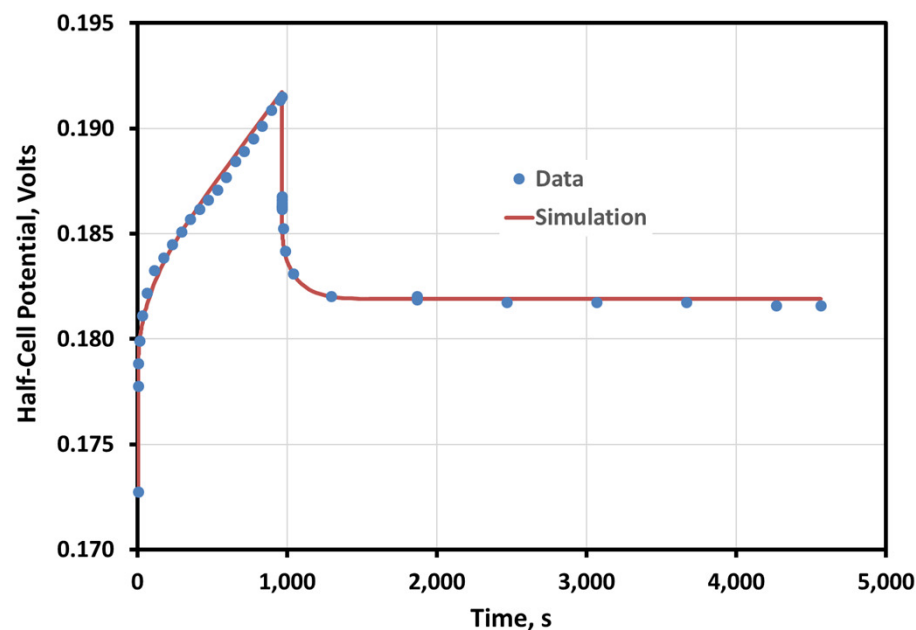
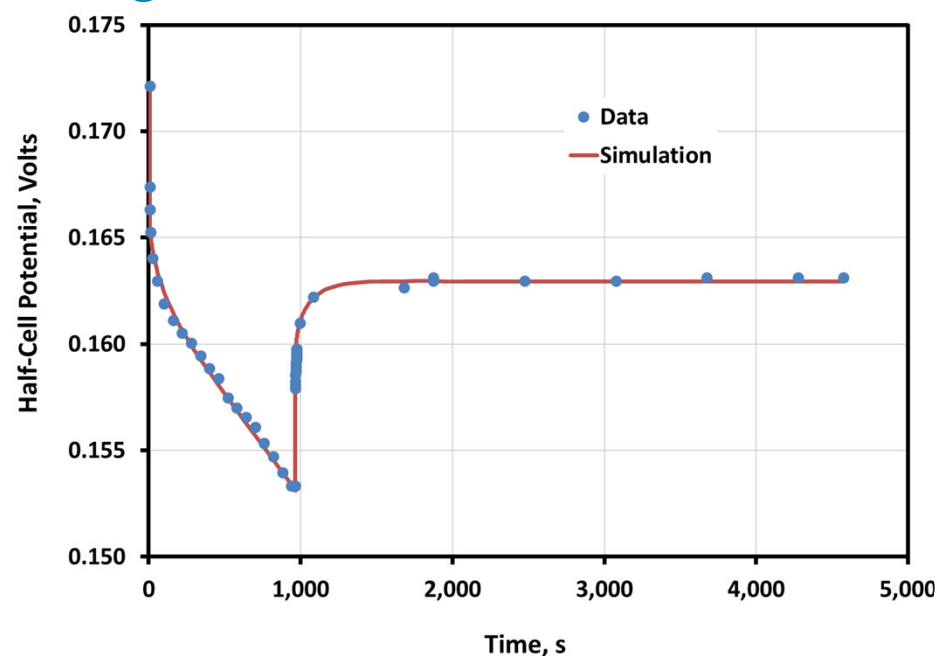
C/18 Current for 16 Minutes Followed by 45 Minutes Rest, Repeat



- Assumed thermodynamic functions for single phase regions shown.
- Same Nernst-like function used for all phases but parameters adjusted depending on whether region is more linear or logarithmic in nature.
- Logarithmic behavior of LiC_{12} phase adopted initially because it fit the data better, but region is narrow enough for linear to adequately fit the data

Analysis of Half-Cell Data Indicates Good Stability

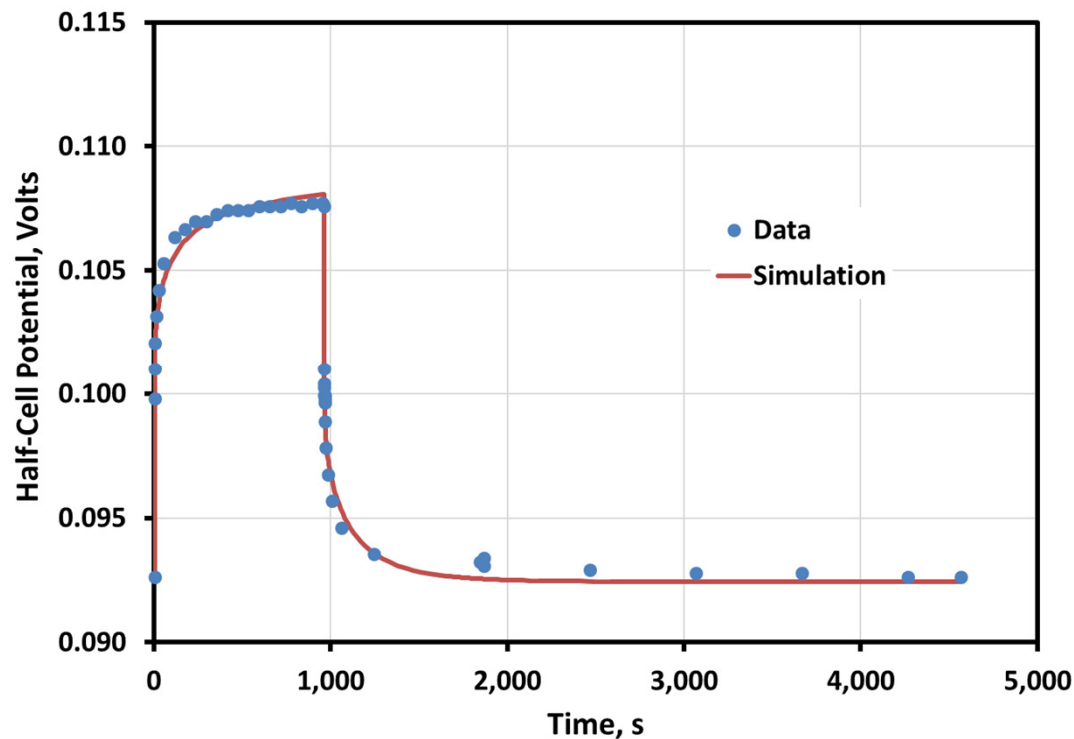
Charge and Discharge A12 Graphite Half-Cell GITT Data in the LiC_{32} Single Phase Taken More than a Week Apart



- Half-cell data can be problematic because the lithium electrode is generally unstable, although it is known to be better behaved at lower currents.
- Both sets of data were fit with an electrochemical half-cell intercalation active material model using the same parameter set indicating a relatively stable cell.
- Diffusion coefficient for the single phases varied from 1.2 to $2.0 \times 10^{-13} \text{ cm}^2/\text{s}$, based on graphite active surface area equal to the BET surface area.

Phase Change Rate Constants Established using the Phase Change Electrochemical Model

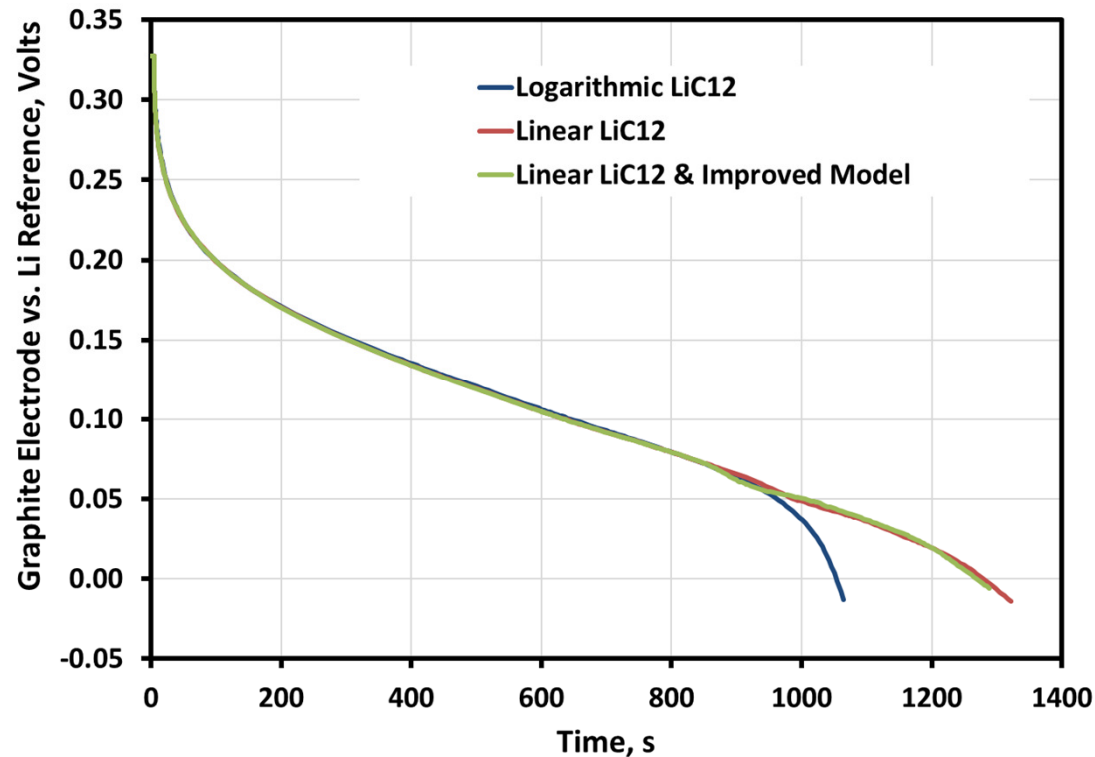
Discharge A12 Graphite Half-Cell GITT Data in the LiC_6 - LiC_{12} Two Phase Region



- The rate of phase change on charge was much faster than discharge.
- Previous studies assumed that the charge and discharge rates were the same.

Simulations Significantly Underperformed Actual Graphite Electrode Experimental Studies

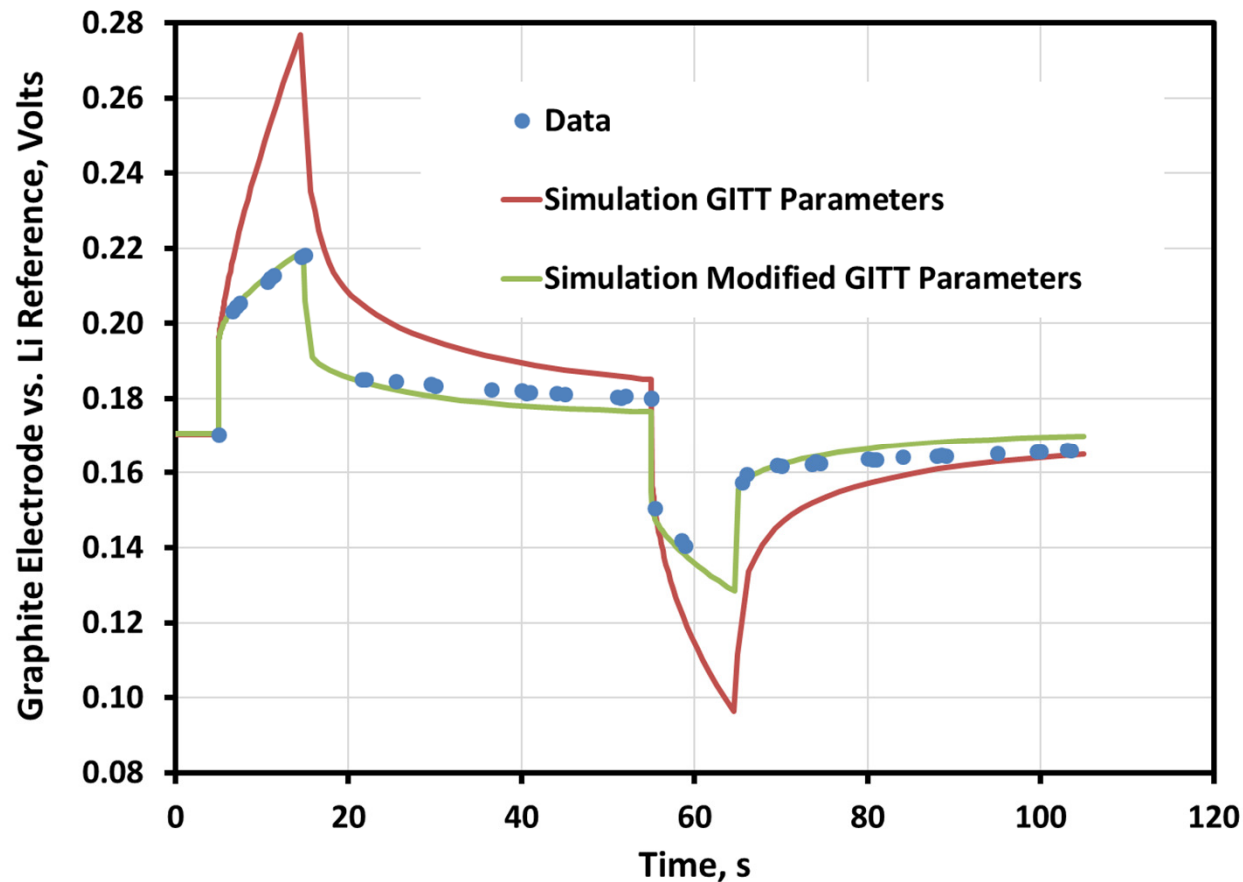
Simulations Using GITT Derived Parameters of A12 Negative Electrode During 1C Charge of a NMC532//Graphite Reference Electrode Cell



- Assumed logarithmic behavior of LiC_{12} phase causes surface potential to drop precipitously as it is formed and lithium surface concentration increases.
- The improved model does not significantly change the charging characteristics.

HPPC-Like Studies Indicated GITT Derived Lithium Diffusion Coefficients too Low

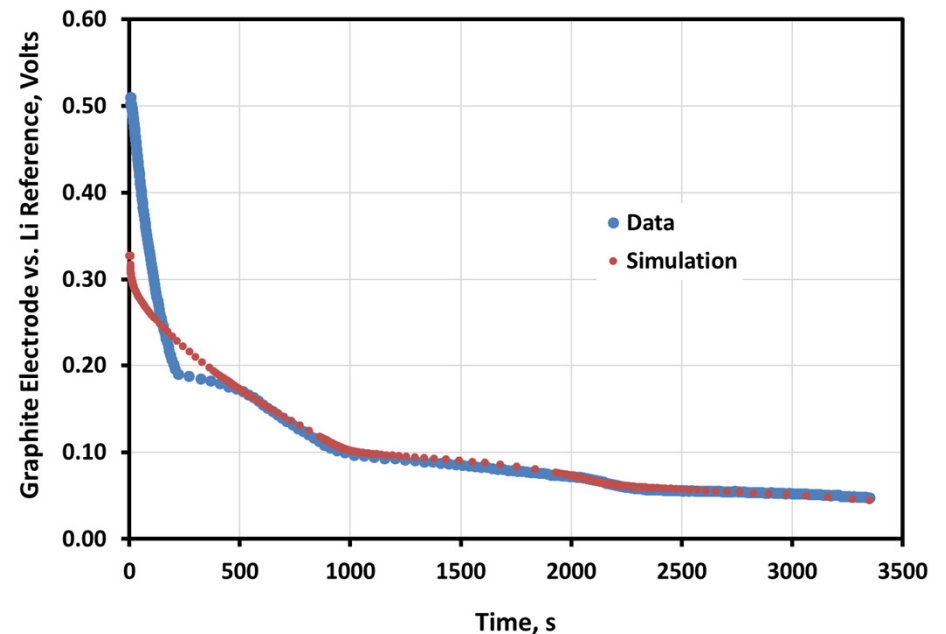
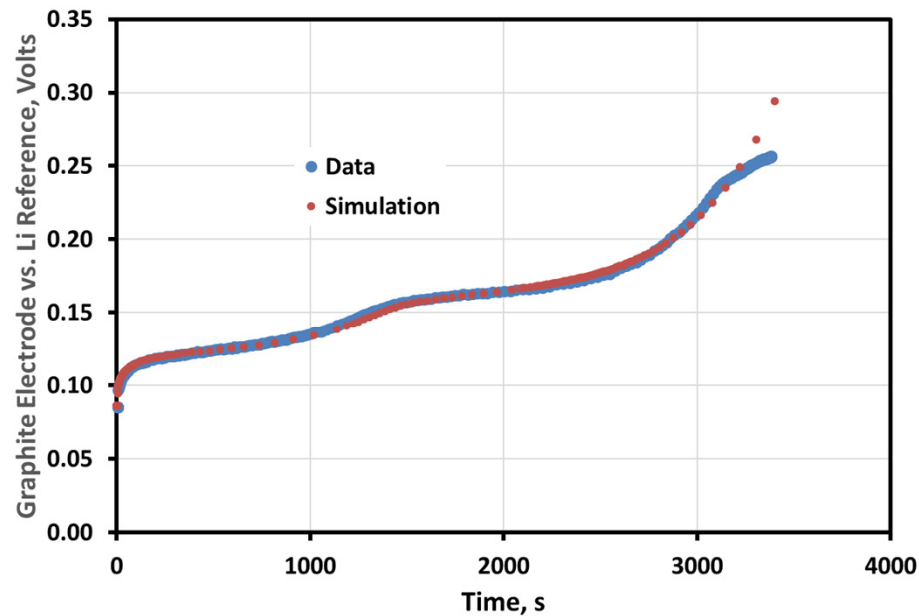
Graphite Electrode Data from 10s 3C Discharge and Charge Pulses on NMC532/Graphite Reference Electrode Cell



- Diffusion coefficient off by more than an order-of-magnitude.

Reference Electrode Cell Data used to Modify Model Parameters

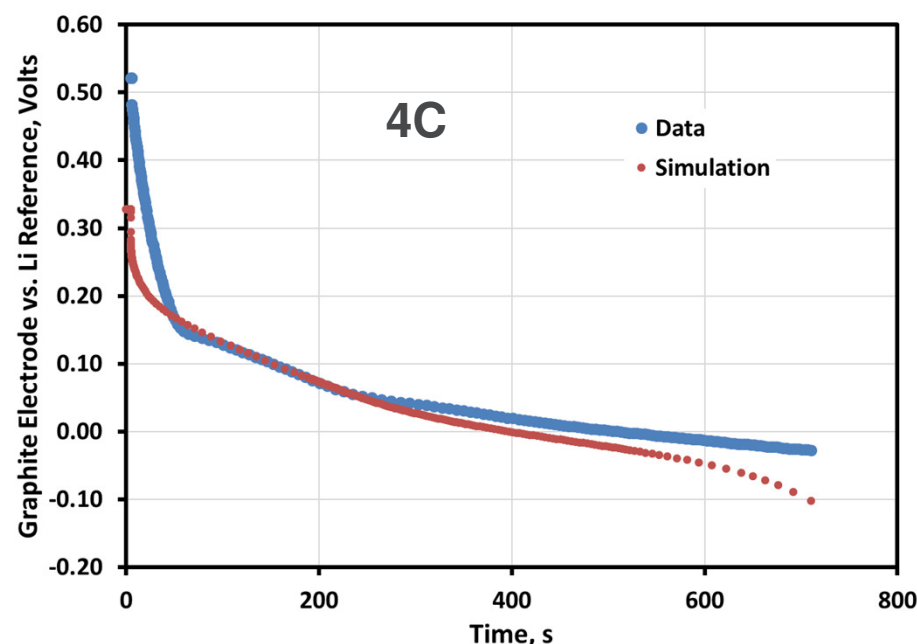
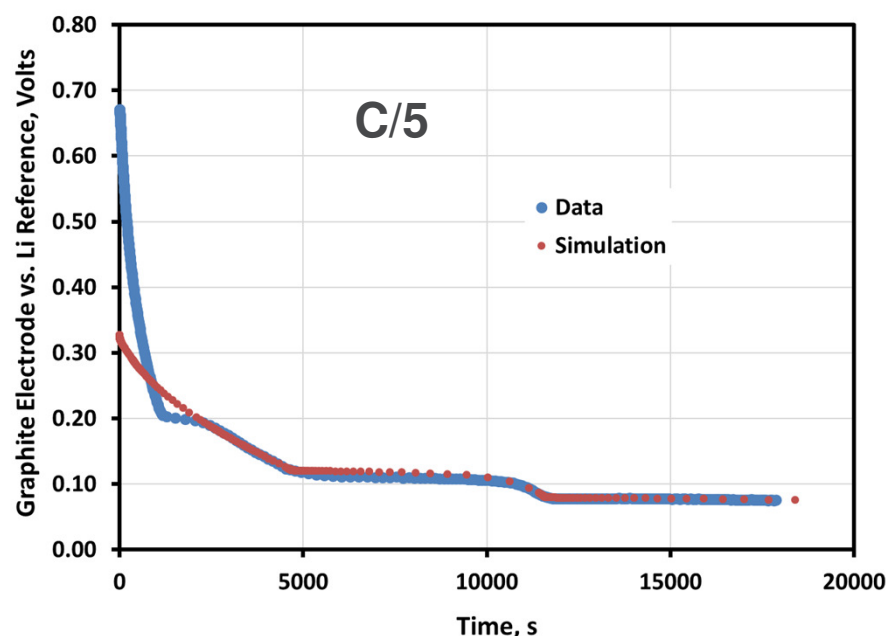
Graphite Electrode Data from 1C Discharge and Charge on NMC532/Graphite Reference Electrode Cell



- Reference electrode cell data crucial to establishing adjusted parameters.
- Modified parameters fit to HPPC pulse and 1C constant current data.
- Diffusion coefficient for the single phases varied from 2.5 to $3.0 \times 10^{-12} \text{ cm}^2/\text{s}$, based on graphite active surface area equal to the BET surface area.

Model with Modified Graphite Parameters can be Used Over a Wide Range of Currents.

Graphite Electrode Data from C/5 and 4C Rate Charges on NMC532/Graphite Reference Electrode Cell



- Agreement at a C/5 rate is excellent, but graphite diffusional effects are relatively small.
- To obtain good agreement at the 4C rate, the diffusion coefficients for the LiC_{12} and LiC_6 phases would have to be increased another order-of-magnitude.
- The variance could also be attributed to lithium plating in part of the cell.

REMAINING CHALLENGES AND BARRIERS

- Understand the fundamental phenomena for apparent increase in lithium diffusion coefficient in graphite at higher rates.
- Development of a more detailed SEI model and lithium side reaction for an electrochemical model describing lithium plating.
- Establish fast charge limitations.

PROPOSED FUTURE RESEARCH

- GITT data and reference electrode cell studies for other graphites and electrode thicknesses will be examined.
- Fundamental reason for apparent increase in lithium diffusion coefficient at higher rates will be explored.
- A more detailed SEI model will be developed and a lithium side reaction will be added to the model to describe lithium plating.
- Integrate model developments with multi-scale multi-domain modeling effort (BAT339).
- Exercise model to examine fast charge limitations.

Any proposed future work is subject to change based on funding levels.

SUMMARY

- Graphite active materials were shown to be better described with the electrochemical model previously developed that includes the phase-transition phenomena as well as lithium intercalation.
- The graphite electrode electrochemical model was effectively used to simulate GITT studies on half-cells.
- Similar modeling results was obtained in comparison to earlier GITT studies on a different type of graphite.
- Attempts to improve the electrochemical model did not significantly increase its high current rate capability.
- Applying the advanced electrode model to a broad range of graphite electrode half-cell and reference electrode cell data indicates the lithium diffusion coefficient for graphite is a strong function of applied current (i.e. GITT @ C/18 vs. HPPC @ 3C).
- A single parameter set can be used to simulate the graphite electrode from between around C/5 and 4C.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Three National Laboratories have teamed to form this integrated effort focused on enabling fast charge capability.
- This effort is part of a broad range of unified studies (BAT338, BAT339, BAT340, BAT341, and BAT371).

RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

- This project was initiated after the last review and therefore has no previous year reviewers' comments.

ACKNOWLEDGMENT

- Support for this work from Battery R&D, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Samm Gillard, Steven Boyd, and David Howell